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Covalently Chemical Modification of Lithium Ion-Encapsulated Fullerene: Synthesis and Characterization of $[Li^+@PCBM]PF_6^-$

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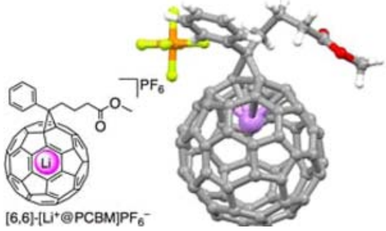
ABSTRACT



Covalently organic derivatization of $[Li^+@C_{60}]PF_6^-$ to obtain Li^+-encapsulated PCBM, $[Li^+@PCBM]PF_6^-$, is described. Synthetic procedures, electrochemical properties, light absorption properties, details of isomerization from [5,6]- to [6,6]-isomer, and X-ray crystal structure of $[Li^+@PCBM]PF_6^-$ are discussed.

Production of lithium-encapsulated [60]fullerene, $Li@C_{60}$, with injection of lithium plasma into C_{60} was first investigated by Campbell et al. in 1996.[1−3] Lithium-ion-encapsulated [60]fullerene, $[Li^+@C_{60}]$ salt, was then synthesized in pure form and structurally characterized by X-ray diffraction analysis in 2010.[4,5] Recently, host−guest complexes of $[Li^+@C_{60}]PF_6^-$ and calix[4]pyrroles (or porphyrins) have been investigated to study the electron transfer processes involved.[6,7] However, covalent chemical modifications of $[Li^+@C_{60}]PF_6^-$ are still eagerly awaited since such covalent functionalization is expected to produce new functional materials for applications not only in chemistry but also in applied physics and biology.

Chemical modification of fullerenes plays a significant role in fullerene-based materials research,[8] including the expanding field of organic photovoltaics.[9] In particular,

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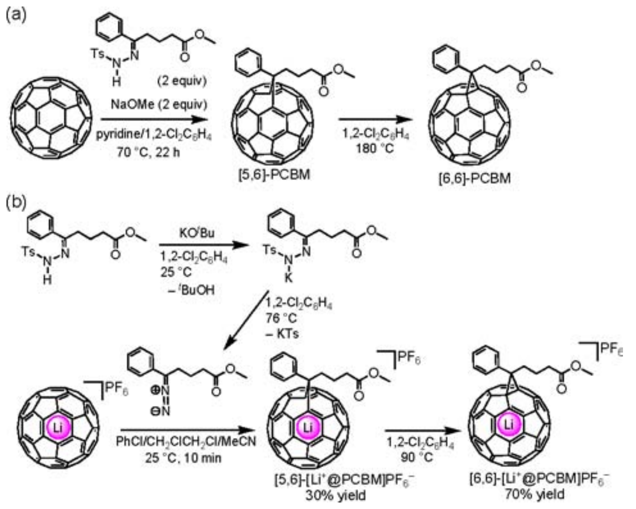
[6,6]-phenyl-C61-butyric acid methyl ester (PCBM)[10−12] could be considered as one of the most defining fullerene derivative, and it is widely used as an electron acceptor in organic thin-film photovoltaic cells.[13] Thus, we anticipate that the Li^+-encapsulated version of PCBM will serve as an attractive material for organic photovoltaics since encapsulation of a lithium ion into the fullerene cage will drastically alter the electronic property of PCBM. Herein we report the synthesis of a PCBM-type compound, $[Li^+@PCBM]PF_6^-$, to represent the covalent organic functionalization of $[Li^+@C_{60}]PF_6^-$. Accordingly, we report the synthetic procedures, properties, and X-ray structures of [6,6]-adducts of $[Li^+@PCBM]PF_6^-$.

Chemical modification of $[Li^+@C_{60}]PF_6^-$ was first attempted according to reported procedures[10] for the synthesis of PCBM, which involves the reaction of C_{60} with tosyl hydrazone ($PhC({=}NNHTs)CH_2CH_2CH_2CO_2Me$) and NaOMe in a pyridine/1,2-dichlorobenzene solution (Scheme 1a). However, the desired product did not form under such conventional conditions; instead, the reaction resulted in a complex mixture, attributed to the higher reactivity of $Li^+@C_{60}$ as compared to C_{60}, as well as the ionic nature of the PF_6^- counteranion. After extensive screening, we found that the use of diazoalkane ($PhC({=}NN)CH_2CH_2CH_2CO_2Me$), in place of tosyl hydrazone, afforded the desired PCBM product in 30% isolated yield (Scheme 1b). This diazoalkane could be readily prepared by treatment of tosyl hydrazone with KO^tBu in 1,2-dichlorobenzene to obtain tosyl hydrazone salt $PhC({=}NNKTs)CH_2CH_2CH_2CO_2Me$, followed by heating to eliminate potassium tosylate (KTs) and subsequently washing with water using a separating funnel to remove KTs entirely. We consider the removal of KTs is necessary since the tosylate anion (Ts^-), in particular, would hinder the formation of the target compound, $[Li^+@PCBM]PF_6^-$, due to exchange of the counteranion.

Scheme 1. Synthesis of PCBMs[a]



[a] Conditions: (a) Synthesis of ordinary PCBM. Tosyl hydrazine is used for the synthesis. (b) Synthesis of Li^+-encapsulated PCBM by using diazoalkane.

In order to monitor the reaction and to isolate the product, we had to adopt suitable conditions for the HPLC analysis and separation, respectively. After considerable examination, we selected a Cosmosil Buckyprep column (Nacalai Tesque) with an unusual eluent system of 1,2-dichlorobenzene and acetonitrile (95:5 v/v) containing 50 mM tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) for analysis and that of chlorobenzene, 1,2-dichloroethane, and acetonitrile (50:35:15 v/v/v) containing saturated tetramethylammonium hexafluorophosphate (Me_4NPF_6) for separation. In the absence of ammonium salts, the chromatography failed due to heavy line-tailing and broadening. We surmise that the reason for this would be the oscillation in the interionic distance between $[Li^+@PCBM]$ and PF_6^-; a longer interionic distance allows for better retention of the $[Li^+@PCBM]$ component in the stationary phase and vice versa. Therefore, we considered the addition of excess PF_6^- anion to the eluent itself, so that each $[Li^+@PCBM]$ cation is surrounded by a PF_6^- ionic atmosphere. This strategy would ensure a consistently shorter interionic distance between $[Li^+@PCBM]$ and PF_6^-, thus solving the problem of line-tailing and broadening in the HPLC peaks. For product isolation, we had specifically used a tetramethylammonium cation instead of the tetrabutyl variant since Me_4NPF_6 exhibits a lower solubility in chlorobenzene. This lower solubility allowed for the successful removal of the Me_4NPF_6 salt via extraction of the product. Filtration of this suspension would then yield $[Li^+@PCBM]PF_6^-$ as the filtrate.

The isolated product was then characterized by both spectrometric and spectroscopic analyses. The high-resolution atmospheric pressure chemical ionization (APCI) time-of-flight (TOF) mass spectrum exhibited parent positive ion peaks at $m/z = 917.1146$ for the product (Figure 1a and Figure S3 in Supporting Information). The ^1H NMR data indicated that the product is a [5,6]-isomer (Scheme 1). Small differences in chemical shifts were observed (up to 0.08 ppm) upon comparison of the ^1H NMR data for [5,6]-$[Li^+@PCBM]PF_6^-$ and [5,6]-PCBM (Figure S1). This slight disparity indicates that the encapsulated lithium ion does not induce any significant magnetic effect on the π-system of the fullerene cage. The ^7Li NMR data of [5,6]-$[Li^+@PCBM]PF_6^-$, on the other hand, exhibited a singlet signal at δ −10.7 in 1,2-dichlorobenzene, which is downfield compared to the signal of the starting material $[Li^+@C_{60}]PF_6^-$ (δ −11.2) (Figure S2). This result suggests that the shielding effect on the encapsulated lithium ion was weakened due to the change in the fullerene π-system.

Next, we investigated the reaction conditions for the isomerization of the [5,6]-isomer to the [6,6]-isomer. The heating of [5,6]-$[Li^+@PCBM]PF_6^-$ in 1,2-dichlorobenzene at 90 °C for 22 h successfully produced

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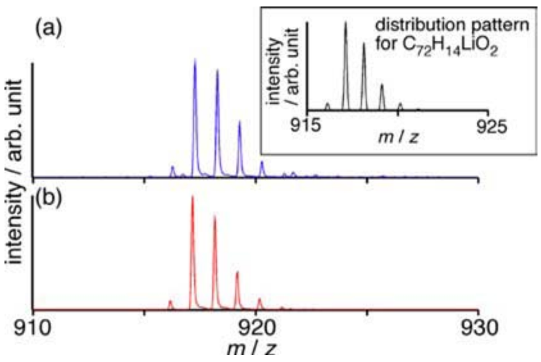
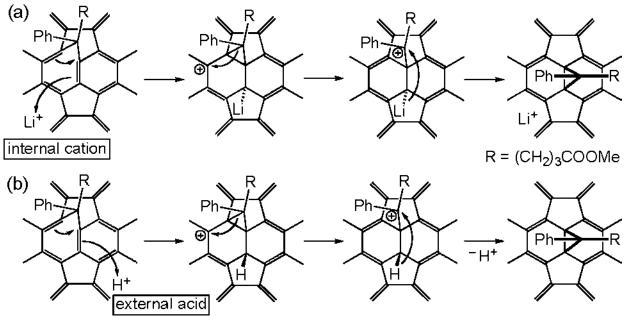


Figure 1. APCI-TOF mass spectra for (a) [5,6]-$[Li^+@PCBM]PF_6^-$ (blue line) and (b) [6,6]-$[Li^+@PCBM]PF_6^-$ (red line).

[6,6]-$[Li^+@PCBM]PF_6^-$ in 70% isolated yield (Scheme 1b). We treated "empty" [5,6]-PCBM under the same reaction conditions and confirmed that the isomerization did not occur at this temperature. We postulate that the encapsulated lithium ion lowers the activation energy of this reaction (Scheme 2). This proposed mechanism involves a tertiary cationic species at the fullerene cage (Scheme 2a), which had also been similarly suggested for the acid-catalyzed isomerization mechanism for empty PCBM (Scheme 2b).[11] A difference between the two mechanisms is the addition of an internal cation or external acid to the fullerene double bonds. Note that the former case (Scheme 2a) may involve a slightly concave sp^3 fullerene carbon atom at their intermediate states. Such lithium ion−carbon interaction likely exists, judged from the position of the Li^+ ion in the X-ray structure of [5,6]-$[Li^+@PCBM]PF_6^-$ (vide infra). In any event, this is a rare example that reports the comparison of chemical reactivity between encapsulated and empty fullerenes possessing the same fullerene cage (i.e., C_{60}).[14] The isomerized product, [6,6]-$[Li^+@PCBM]PF_6^-$, was characterized by high-resolution APCI-TOF mass spectrometry (m/z = 917.1151, Figures 1b and S6) as well as ^1H and ^7Li NMR measurements. For the ^7Li NMR measurement, the signal for the encapsulated Li^+ of [6,6]-$[Li^+@PCBM]PF_6^-$ (δ −12.3) experienced an upfield shift compared to that of $[Li^+@C_{60}]PF_6^-$ (δ −11.2). This upfield shift is in good agreement with the observations made for other endohedral fullerenes such as $H_2@C_{60}$ and $He@C_{60}$ that had undergone [6,6]-addition.[15,16]

In addition, the electrochemical and photophysical properties of [5,6]- and [6,6]-$[Li^+@PCBM]PF_6^-$ were investigated. Electrochemical studies revealed high electron affinity of these compounds: [5,6]- and [6,6]-$[Li^+@PCBM]PF_6^-$ exhibited the first reduction potentials at −0.37 and −0.43 V vs Fc/Fc^+, respectively (Figure 2), which are much higher than those of empty PCBM (−1.16 and −1.18 V vs Fc/Fc^+ for [5,6]- and [6,6]-PCBM, respectively). Note that the reduction potential of $[Li^+@PCBM]$ is close to that of $[Li^+@C_{60}]$, as shown in Table 1, which is different from the case for empty PCBM and C_{60}. These facts are explained with large contribution of the Li^+ ion on reduction of the compound, compared with contribution of the fullerene cage. UV−vis spectra of these compounds were similar to those of the respective PCBMs, albeit slightly broadened (Figure S7); the broader peaks are most likely due to partial aggregation of Li^+-encapsulated PCBMs in 1,2-dichlorobenzene. Overall, encapsulated Li^+ does not affect the light absorption property of the C_{60} cage but exerts a heavy influence on its electron affinity. The latter shows that a static electric field induced by Li^+ ion stabilizes the LUMO of the outer PCBM cage.

Scheme 2. Proposed Mechanism for the Thermal Isomerization[a]



[a] Conditions: (a) Internal lithium-ion-catalyzed mechanism for conversion from [5,6]- to [6,6]-isomer. (b) Acid-catalyzed mechanism propsed in ref 11.

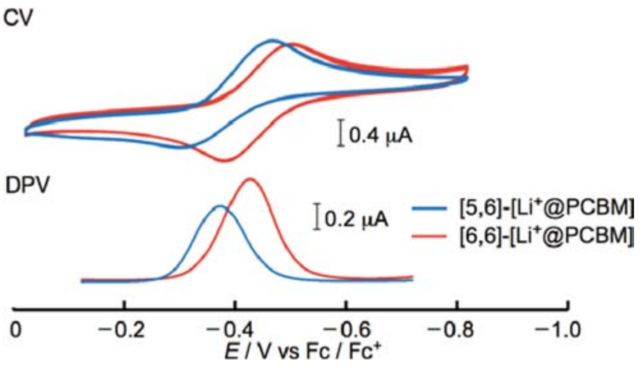


Figure 2. Cyclic voltammograms (CV) and differential pulse voltammograms (DPV) in 1,2-dichlorobenzene containing 50 mM Bu_4NPF_6 for [5,6]-$[Li^+@PCBM]PF_6^-$ (blue line) and [6,6]-$[Li^+@PCBM]PF_6^-$ (red line).

Finally, we performed X-ray crystallographic analysis of [6,6]-$[Li^+@PCBM]PF_6^-$ to determine its unambiguous structure (Figure 3a).[17] The Li^+ ion was located in one position at 93 K under the [6,6]-bond (Figure 3b) with interatomic distance of 2.23 and 2.34 Å for C−Li^+.

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Table 1. Reduction Potentials of Li^+-Encapsulated and Empty PCBMs[a]

	reduction potential [V vs Fc/Fc^+]		
	Li^+-encapsulated	empty fullerenes	encapsulation-induced shift
C_{60}	−0.37	−1.08	+0.71 V
[5,6]-PCBM	−0.37	−1.16	+0.79 V
[6,6]-PCBM	−0.43	−1.18	+0.75 V

[a] First reduction potentials determined by DPV.

This was in contrast to the case of the $[Li^+@C_{60}]PF_6^-$ crystal, where the Li^+ ion was located in the 2-position under six-membered rings at 22 K.[5] This spatial position adopted by Li^+ in $[6,6]$-$[Li^+@PCBM]PF_6^-$ is probably in accordance with the direction of the molecular dipole moment. Theoretical calculation of the empty [6,6]-PCBM at the B3LYP/6-31G level revealed the dipole moment from the C_{60} cage ($\delta+$) to the organic addend ($\delta-$) (Figure S12). We consider that the Li^+ ion is located at the organic addend side to cancel the dipole moment partially. The PF_6^- counteranion was located closely to the cationic component (Figure 3c); the distance between lithium and phosphorus atoms was 6.24 Å. Crystal packing structure displayed a layer-by-layer structure of cationic and anionic sheets (Figure 3d).

In conclusion, we have investigated the chemical modification of $[Li^+@C_{60}]PF_6^-$ by demonstrating the synthesis of a PCBM-type compound, $[Li^+@PCBM]PF_6^-$. We have successfully prepared [5,6]- and [6,6]-isomers of $[Li^+@PCBM]PF_6^-$, whose structures and properties were elucidated. The present study will provide new insights into the reactivity of $[Li^+@C_{60}]PF_6^-$ for carbon cluster research[18−22] and development of photovoltaics,[23−25] as well as for studies in other fields.

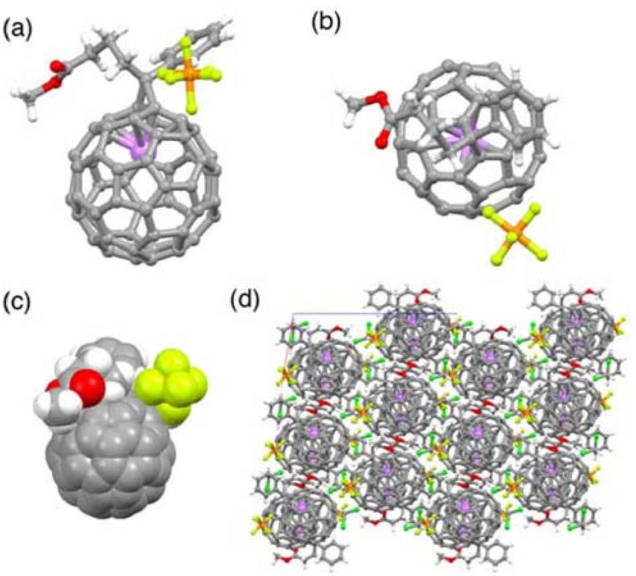

Figure 3. X-ray crystallographic structure of $[6,6]$-$[Li^+@PCBM]PF_6^-\cdot(CH_2Cl_2)$. (a) Ball-and-stick drawing of the molecular structure, side view. (b) Top view. (c) CPK model of adjacent cationic and anionic parts. (d) Crystal packing structure.

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Supporting Information Available. Synthetic procedures and NMR, MS, UV−vis, CV, X-ray crystallography, and DFT calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) The crystal contains a set of disordered atoms (Figure S9). Optimized occupancy was 0.72:0.28. Due to this disordered issue, thermal parameters of non-hydrogen atoms were refined isotropically. An ORTEP drawing is presented in Supporting Information (Figure S10).

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The authors declare no competing financial interest.